Direct Observation of Oxidative Cyclization of η^2-Alkene and η^2-Aldehyde on Ni(0) Center. Significant Acceleration by Addition of Me₃SiOTf

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Carbonyl compounds are transformed into various organic compounds having an oxygen functional group by transition metal-catalyzed or -mediated reactions. Recently, nickel-catalyzed multi-component coupling reactions involving carbonyl compounds have received increasing attention.[1a−h] Among several reaction mechanisms proposed for these processes, the oxidative cyclization involving metal, C=O, and C=C (or C≡C) bonds represents one of the most often envisaged, yet never directly demonstrated, key steps.[1a−g,2] Here, we report the first direct observation of oxidative cyclization by η^2-aldehyde and η^2-alkene ligands with Ni(0). Moreover, we also observed the significant acceleration of such cyclization by electrophilic addition of Me₃SiOTf to carbonyl oxygen, which may have potential relevance to the course of some coupling reactions involving carbonyl compounds and Lewis acidic substrates.[3]

The addition of 5-hexenal or o-allylbenzaldehyde to a solution of Ni(cod)₂ and PR₃ (1 equiv) gave (η^2:η^2-CH₂=CH(CH₂)₃CHO)-Ni(PCy₃) (**1a**) or (η^2:η^2-CH₂=CHCH₂C₆H₄CHO)Ni(PR₃) (**1b,c**) quantitatively (Scheme 1). The chemical shifts of vinyl and formyl groups in ¹H and ¹³C NMR of **1a** are in much higher magnetic fields than those of 5-hexenal, which suggests that both C=C and C=O double bonds coordinate to the nickel(0) center.[4] Heating the solution of **1** at 60 or 80 °C resulted in oxidative cyclization to give nickelacycle complexes (**2**).[5] Even at room temperature for 16 h, **1c** underwent oxidative cyclization in 68% yield. For **2a**, only the syn isomer was obtained, the structure of which was determined by X-ray diffraction analysis, while **2b** and **2c** existed as two isomers. The structure of **2b-anti** was also confirmed by X-ray diffraction analysis (Figure 1). Under a carbon monoxide pressure (3 atm), a mixture of syn and anti isomers of **2b** or **2c** reacted with carbon monoxide to give the corresponding lactone **3** as a sole product quantitatively concomitant with the formation of Ni(CO)ₙ(PR₃)₄₋ₙ.[6] To the best of our knowledge, the direct observation of oxidative cyclization from the η^2-carbonyl:η^2-olefin coordination complex to five-membered metallacycle has not been reported even with early transition metal systems. The addition of 2 equiv of PPh₃ to Ni(cod)₂ and o-allylbenzaldehyde did not give **1c** but instead gave the η^2-aldehyde bisphosphine complex (**1c′**).[7] In contrast to **1c**, **1c′** did not undergo oxidative cyclization at room temperature for 24 h at all, which could be attributable to the failure of simultaneous coordination of both C=C and C=O bonds to nickel.

Previously, we reported that Lewis acid (e.g., Me₃Al) or Me₃-SiOTf can add to the carbonyl group in enone coordinated to palladium(0) to enhance the reactivity of the enone toward carbon nucleophile and disilane.[8] We now found the addition of 1 equiv of Me₃SiOTf to η^2:η^2-enal complexes **1a−c** at room temperature accelerated the cyclization significantly to give η^1:η^1-3-siloxypropyl complexes (**4a−c**) quantitatively (Scheme 2, Figure 2).[9] Without adding Me₃SiOTf, cyclization of **1** was much slower (see Scheme 1). Moreover, the reaction of **2b** with Me₃SiOTf proceeded only
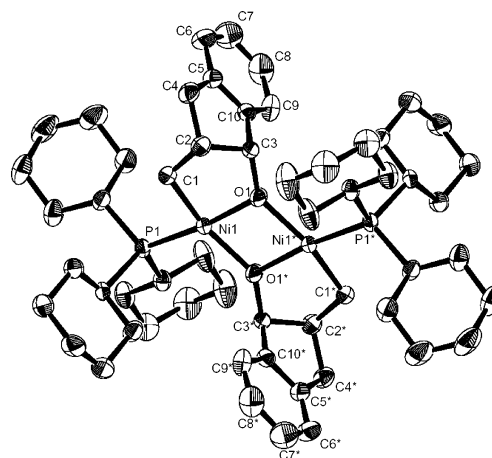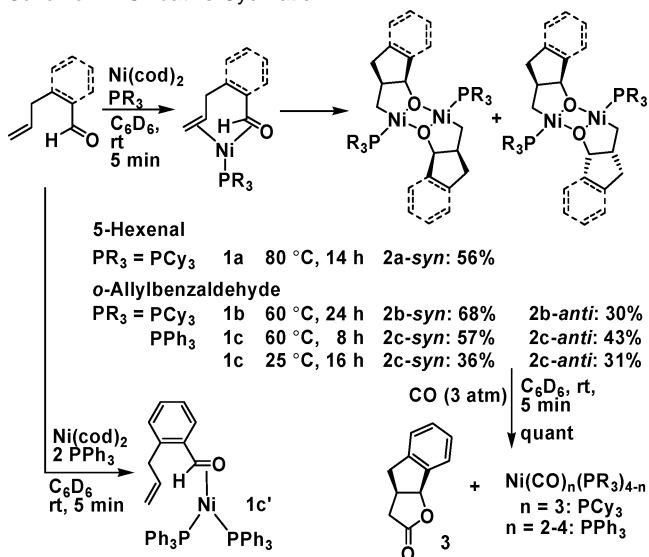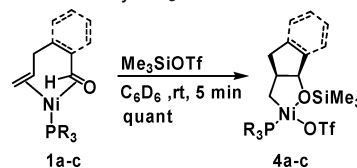

Figure 1. Molecular structure of **2b-anti**.

Scheme 1. Oxidative Cyclization

5-Hexenal
PR₃ = PCy₃ **1a** 80 °C, 14 h **2a-syn**: 56%

o-Allylbenzaldehyde
PR₃ = PCy₃ **1b** 60 °C, 24 h **2b-syn**: 68% **2b-anti**: 30%
      PPh₃ **1c** 60 °C, 8 h **2c-syn**: 57% **2c-anti**: 43%
            1c 25 °C, 16 h **2c-syn**: 36% **2c-anti**: 31%

Scheme 2. Acceleration by Me₃SiOTf

very slowly to generate a trace of **4b** at 50 °C for 2 h. These results suggest that the Si−O bond formation takes place prior to cyclization, presumably via attack of Me₃SiOTf at the oxygen of the η^2-coordinated C=O group. To examine if Me₃SiOTf reacts with the C=O double bond coordinated to nickel(0), the reaction of Me₃SiOTf with RCHO (R = Ph, ᵗBu) under similar reaction conditions was carried out.
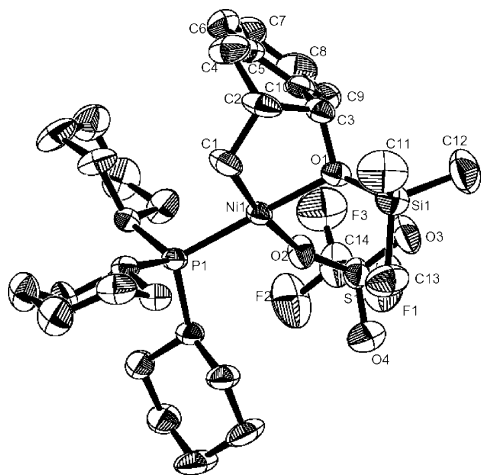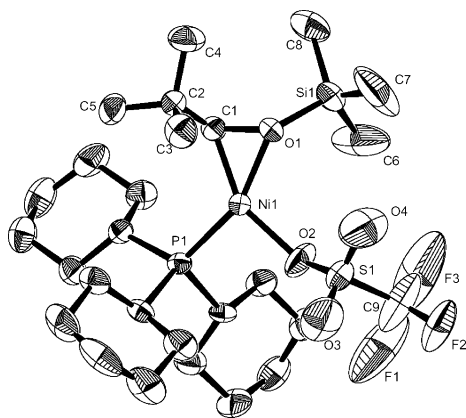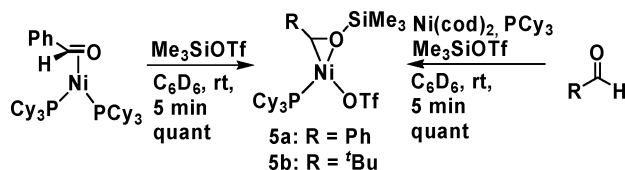
Figure 2. Molecular structure of **4b**.

Figure 3. Molecular structure of **5b**.

Scheme 3. Addition of Me$_3$SiOTf to η^2-RCHO

Treatment of (η^2-PhCHO)Ni(PCy$_3$)$_2$[10] with Me$_3$SiOTf gave (η^1:η^1-Me$_3$SiOCH(Ph))Ni(PCy$_3$)OTf (**5a**) quantitatively, concomitant with dissociation of PCy$_3$ (Scheme 3).[11] **5a** was also prepared by the treatment of PhCHO with Me$_3$SiOTf in the presence of Ni(cod)$_2$ and PCy$_3$. Similarly to the latter method, (η^1:η^1-Me$_3$-SiOCH(^{t}Bu))Ni(PCy$_3$)OTf (**5b**) was prepared, the structure of which was confirmed by X-ray diffraction analysis (Figure 3). The complex shows a square planar structure with the siloxymethyl ligand generated by the electrophilic addition of Me$_3$SiOTf to carbonyl oxygen. An intermolecular reaction of **5a** with styrene or trimethylvinylsilane was attempted, but in vain. Presumably, the formation of an intermediate for the cyclization having neighboring η^2-olefin and siloxymethyl ligands from **5** may have been unfavorable. On the other hand, the cyclization from **1** to **4** may involve the preorganized C=C and C=O double bonds on the nickel(0) center, which are ready to undergo the Me$_3$SiOTf-triggered multibond formation process.

In conclusion, we have demonstrated the formation of nickelacycle by the direct oxidative cyclization of (η^2:η^2-CH$_2$=CHCH$_2$-CH$_2$CH$_2$CHO)Ni(PR$_3$) or (η^2:η^2-o-CH$_2$=CHCH$_2$-C$_6$H$_4$CHO)-Ni(PR$_3$) and the drastic acceleration of cyclization by the addition of Me$_3$SiOTf. (η^2-PhCHO)Ni(PCy$_3$)$_2$ also reacted with Me$_3$SiOTf

to generate a nickel−carbon bond quantitatively. The observations in this paper suggest that any reagent having Lewis acidic character present in the reaction medium could be a promoter for the cyclization involving C=O and C=C double bonds coordinated to a nickel(0) center

Supporting Information Available: Experimental procedures (PDF) and crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) It was suggested that the coordination of a Lewis acidic reagent to a carbonyl group on nickel enhances the reactivity of the carbonyl compound.[1f]

(4) Selected spectral data for **1a**. ^{1}H NMR (C$_6$D$_6$): δ 0.60 (m, 1H), 0.83 (m, 1H), 0.95−2.28 (m, 36H, including 1H of −C**H**=CH$_2$ at δ 2.00), 2.31 (t, J = 8.0 Hz, 1H, −CH=C**H**$_2$), 2.46 (m, 1H, −C**H**$_2$CH=CH$_2$), 3.01 (m, 1H, −C**H**=CH$_2$), 5.54 (m, 1H, −C**H**O). ^{31}P NMR (C$_6$D$_6$): δ 38.4 (s). ^{13}C NMR (C$_6$D$_6$): δ 45.8 (d, J_{CP} = 3.8 Hz, −C**H**=CH$_2$), 68.2 (d, J_{CP} = 8.4 Hz, −C**H**=CH$_2$). 102.9 (d, J_{CP} = 7.6 Hz, −C**H**O). Anal. Calcd for C$_{24}$H$_{43}$O$_1$P$_1$Ni$_1$: C, 65.92; H, 9.91. Found: C, 64.99; H, 9.64.

(5) Selected spectral data for **2b-anti**: ^{1}H NMR (C$_6$D$_6$): δ −0.51 (m, 1H of −C**H**$_2$Ni), 0.90−2.25 (m, 34H, including 1H of −C**H**$_2$Ni at δ 1.45), 2.45 (m, 1H, −C**H**CH$_2$C$_6$H$_4$−), 2.98 (dd, J = 15.1 Hz, J = 5.7 Hz, 1H, −C**H**$_2$C$_6$H$_4$−), 3.01 (m, 1H, −C**H**$_2$C$_6$H$_4$−), 4.55 (m, 1H, −NiCH$_2$CHC**H**O−), 7.22 (d, J = 7.6 Hz, 1H), 7.34 (t, J = 7.0 Hz, 1H), 7.81 (t, J = 7.3 Hz, 1H), 10.02 (d, J = 7.3 Hz, 1H). ^{31}P NMR (C$_6$D$_6$): δ 28.6 (s). Anal. Calcd for C$_{28}$H$_{43}$Ni$_1$O$_1$P$_1$(C$_6$H$_6$)$_{0.5}$ C, 71.01; H, 8.84. Found: C, 70.60; H, 8.91.

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(7) Selected spectral data for **1c′**. ^{1}H NMR (C$_6$D$_6$): δ 2.87 (brd, J = 5.4 Hz, 2H), 3.88 (brd, J = 14.5 Hz, 1H, −C**H**=CH$_2$), 4.04 (brd, J = 10.0 Hz, 1H, -C**H**=CH$_2$), 5.11 (brm, 1H, −CH=C**H**$_2$), 6.60 (brs, 1H, −C**H**O). ^{31}P NMR (C$_6$D$_6$): δ 29.0 (brs). The olefinic proton chemical shifts in **1c′** are apparently different from those of **1c**: ^{1}H NMR (C$_6$D$_6$) δ 2.38 (brd, J = 13.0 Hz, 1H, −C**H**=CH$_2$), 2.59 (brd, J = 8.1 Hz, 1H, −CH=C**H**$_2$), 2.90 (brs, 2H), 4.11 (brm, 1H, −C**H**=CH$_2$), 6.80−7.10 (br, 11H, including −C**H**O).

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(9) Selected spectral data for **4b**. ^{1}H NMR (C$_6$D$_6$): 0.03 (dt, J = 10.3 Hz, 1.5 Hz, 1H, −CH$_2$Ni), 0.57 (s, 9H, −OSi**Me**$_3$), 0.86 (t, J = 8.9 Hz, 1H, −C**H**$_2$Ni), 1.30−1.92 (m, 34H, including 1H of −NiCH$_2$C**H**− at δ 1.48), 2.67 (d, J = 15.6 Hz, 1H, −C**H**$_2$C$_6$H$_4$−), 2.87 (dd, J = 15.6 Hz, 7.3 Hz, 1H, −C**H**$_2$C$_6$H$_4$−), 4.83 (d, J = 6.4 Hz, 1H, −C**H**OSiMe$_3$), 7.20 (d, J = 7.3 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.53 (t, J = 7.3 Hz, 1H), 8.12 (d, J = 7.6 Hz, 1H). ^{31}P NMR (C$_6$D$_6$): δ 32.9 (s). Anal. Calcd for C$_{32}$H$_{52}$F$_3$-Ni$_1$O$_4$S$_1$Si$_1$P$_1$: C, 54.32; H, 7.41. Found: C, 54.08; H, 7.38.

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(11) Selected spectral data for **5a**. ^{1}H NMR (C$_6$D$_6$): δ 0.31 (s, 9H, −OSi**Me**$_3$), 0.95−1.95 (m, 33H), 4.34 (d, J_{HP} = 3.5 Hz, 1H, −C**H**OSiMe$_3$), 7.00 (m, 3H), 7.47 (d, J_{HP} = 7.3 Hz, 2H). ^{31}P NMR (C$_6$D$_6$): δ 42.0 (s).

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